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13. ABSTRACT (Maximum 200 Words) Over the report period, an optical laboratory for characterization materials for frequency domain optical storage was upgraded. Spectral and spectral hole burning properties were studied for several free- based and metallo-naphthalocyanine derivatives in polymer hosts. These materials exhibit a strong 0-0 absorption band and persistent hole burning in the region 800 nm. Hole burning parameters were determined for eight materials; in particular, the hole burning kinetics was analyzed and the quantum efficiencies were determined to be between 0.1% and 1%. Holograms (data pages) in the transmission geometry were successfully recorded in the materials studied using single frequency laser diodes. A photoluminescence of five natural diamonds (type Ia) implanted with Xe ions with dose range 1×10^{13} - 5×10^{14} cm ⁻² was investigated as a function of thermal annealing at temperatures between 300 and 1400 C.		
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**Optical Hole Burning Studies of Materials for Frequency Domain Optical Storage and
Processing**

March 25, 2002

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Materials are one of the key elements to advance the spectral hole-burning (SHB) technology for optical storage and processing. Our research is directed to evaluation of some prospective materials for optical hole-burning frequency and time-domain storage applications.

Major focus was on investigation of several naphthalocyanine and octabutoxy phthalocyanine compounds embedded in polymer hosts and on optical characterization of some ion implanted diamonds as actual materials. To characterize and compare different potential hole burning materials, we determined some material parameters including excited state optical lifetime, inhomogeneous linewidth, homogeneous linewidth, hole lifetime, persistent hole annealing temperature, and some others. Special attention was paid to the determination of the quantum yield of hole-burning materials.

Over the report period the progress was achieved in areas of upgrading of laboratory equipment, materials and research.

1. Laboratory

Equipment in our laser and optical spectroscopy laboratory was upgraded to perform spectroscopic research and to characterize hole-burning materials. Major spectroscopic equipment including Perkin Elmer Lambda 900 UV/VIS/NIR Spectrophotometer and the high-resolution double spectrometer Spex 1404 has been purchased and installed. A new Oxford Instruments variable temperature helium cryostat has been purchased and helium pump and pumping line have been installed. This unit allows us to perform measurements at temperatures from 1.4 to 300 K with low level of mechanical vibrations. Hole burning measurements were made with a tunable single frequency CW Ti-sapphire laser (Coherent 899-29). The laser intensity was stabilized at the level of 0.1 %. Detection system consists of lock-in amplifier, monochromator, GaAs cooled photomultiplier, and computer data acquisition board.

2. Materials

The samples under investigation were five naphthalocyanines derivatives: 2,11,20,29-tetra-tert-butyl-2,3-naphthalocyanine ($H_2\text{-TBNP}$), 1,4,8,11,15,18,22,25-octabutoxy-2,3-naphthalocyanine ($H_2\text{-OBNP}$), zinc 2,11,20,29-tetra-tert-butyl-2,3-naphthalocyanine ($Zn\text{-TBNP}$),

nickel 2,11,20,29-tetra-tert-butyl-2,3-naphthalocyanine (Ni-TBNP), and silicon 2,3-naphthalocyanine dioctyloxide (Si-NPDO). To prepare the samples we used two types of host matrix: polyvinyl butyral (PVB) for samples with thickness in the range of 100 to 400 μm , and polystyrene (PS) to produce samples with thickness larger than 1 mm. The doping concentration was between 10^{-3} mol/l and 10^{-5} mol/l.

Diamonds under investigation were five natural diamonds (type Ia) irradiated with 500 keV Xe ions at room temperature over dose range $1 \times 10^{13} - 5 \times 10^{14}$ cm^{-2} . A sample with dose of 5×10^{14} cm^{-2} was subsequently thermally annealed at 1400 C for 2 hours and served as the control sample. Another four sample were annealed gradually (Dr. A.M. Zaitsev) at temperatures between 300 C and 1400 C with increment of 100 C.

3. Research

3.1 Spectral and hole burning properties of naphthalocyanines

Absorption spectra were measured at 8 K in the region of the $S_1 - S_0$ transition. All materials studied have the intense 0-0 band located around 790 nm. Some impurities, particularly H₂-TBNP, display strong signs of aggregation at concentration higher than 10^{-4} mol/l.

Spectral holes were burned in the 0-0 absorption band and detected in transmission by a single frequency tunable Ti: Sapphire laser with linewidth less than 1 MHz at the temperature 1.5 K. To avoid power saturation, low burning intensities between 10 and 200 $\mu\text{W}/\text{cm}^2$ were selected. In addition, for the hole detection the intensity was reduced by two orders of magnitude. To compare different samples, the burning wavelength was chosen to have the initial optical density in all cases at about 0.7. The minimal holewidth (see the Table) was found by extrapolation of the holewidth dependency on burning intensity and on burning time to the zero-intensity zero-exposure limit.

3.2 Determination of quantum efficiency

The measured kinetics were analyzed in order to determine the quantum efficiency of PSHB. We express the quantum efficiency, i.e. ratio of molecules participating in hole burning to the total number of photoexcited molecules, in the parameterized form of $\varphi = \exp(-a)$. We assume that the parameter a is subject to a Gaussian distribution. Taking into account the

dispersion for hole burning kinetics due to the difference in absorption at the laser frequency for centers within the inhomogeneous band, the random orientation of the absorbing centers with respect to the polarization of the burning light, and the distribution of quantum efficiency, the time dependence $H(t)$ of the sample absorption at the peak of the hole can be presented in the form appropriate for the fitting of experimental kinetics. The inhomogeneous broadening Γ_{inh} , was determined from the width of the 0-0 electronic transition in the decomposition fit. We suggest that the homogeneous linewidth Γ_h is half of the determined minimal holewidth since no spectral diffusion was observed in the time range of $10 - 10^5$ seconds. To avoid error due to the hole burning through the phonon sidebands, we fit the experimental kinetics at the initial stages of the hole growth using expression for $H(t)$ with two free distribution parameters, a_c and w . With the distribution parameters a_c and w obtained, we calculated the average quantum efficiency $\langle\phi\rangle$ of PSHB.

Results for all samples studied are shown in the Table. The accuracy of the obtained results was mostly determined by the accuracy of the experimental values of peak absorption cross-section and was estimated to be $\pm 15\%$. Hole burning in all but one free-base system can be described by a single value of the quantum efficiency. Surprisingly, H₂-TBNP at higher concentration shows a distribution of efficiencies, which is likely related to the overlapping of single molecule and aggregate absorption bands at the laser frequency. Three out of four studied metallo-based systems reveal the broad distribution of hole burning efficiency characteristic of a nonphotochemical hole burning. Only Ni-TBNP/PVB displays a single-valued efficiency of about 0.7%. Thus the mechanism is, likely, photochemical, and should be a subject of future investigation. Another interesting result is the very low non-burnable background observed for Si-NPDO, which makes this system useful for holography applications.

Table. Spectroscopic and hole burning parameters for naphthalocyanines doped polymers at 1.5 K.

Sample	Concentration, mole/liter	Holewidth, MHz	Inhomog. Linewidth, MHz	σ_h , cm^2	Efficiency of PSHB, $\langle\varphi\rangle$	Distribution parameters		
						center	width	B
H ₂ -TBNP/PVB	3×10^{-3}	150	1.0×10^7	8.7×10^{-11}	8.9×10^{-3}	5.88	0	0.42
H ₂ -TBNP/PVB	7×10^{-4}	100	1.5×10^7	6.2×10^{-11}	1.3×10^{-3}	6.92	3.5	0.58
H ₂ -TBNP/PS	5×10^{-3}	1150	0.9×10^7	3.2×10^{-12}	3.2×10^{-2}	3.44	0	0.43
H ₂ -OBP/PVB	3×10^{-4}	200	1.6×10^7	4.5×10^{-12}	1.1×10^{-2}	4.51	0	0.57
Zn-TBNP/PVB	2×10^{-4}	380	1.0×10^7	1.7×10^{-11}	1.2×10^{-3}	9.55	6.0	0.28
Zn-TBNP/PS	1.8×10^{-4}	≈ 1000	1.2×10^7	$\approx 4.6\times10^{-12}$	$\approx 1.4\times10^{-3}$	9.16	6.7	0.48
Ni-TBNP/PVB	6×10^{-4}	100	1.5×10^7	2.1×10^{-11}	6.7×10^{-3}	5.00	0	0.67
Si-NPDO/PVB	2×10^{-4}	400	2.0×10^7	8.7×10^{-11}	8.1×10^{-4}	10.06	4.7	0

3.3 Holographic applications of materials studied (Prof. D. Psaltis' group)

Using the prepared samples of Si-N PDO and H₂-TBNP in PVB and PS, we demonstrated the holographic recording of pages of information at low temperature with good fidelity. The light source was a Hitachi 50 mW, temperature controlled laser diode. The reference and signal beams make an angle of 20 degrees outside the sample. The reference consists of a plane wave of 0.2 mW/cm² and is equal to the intensity of the signal. At this intensity, we observed a homogeneous line broadening ~1 GHz for the samples mentioned above.

Holograms were recorded for 4sec in 400 μm thick H₂-TBNP/PVB at 788 nm, 400 μm thick Si-N PDO/PVB at 787nm and 1.5 mm thick H₂-TBNP/PS at 788 nm. The reconstruction from the thick sample shows defects due to non-uniformity. Better optical quality was obtained for the H₂-TBNP in PVB than in the PS matrix. The sample optical densities were 2.0, 2.3, and 7.2 and the absolute diffraction efficiencies were $5 \cdot 10^{-5}$, $7 \cdot 10^{-5}$, and $1.8 \cdot 10^{-6}$, respectively. The low absolute diffraction efficiency is due to lower hole depth and higher absorption. Especially in the case of H₂-TBNP/PVB, the sample with large concentration of $7 \cdot 10^{-4}$ mol/l showed reduced hole depth, probably due to aggregation. We measure a hole depth of 4% with the exposure energy used in the holographic recording.

This preliminary holographic experiment shows that random bit patterns can be recorded in these materials with good fidelity. The relationship between the intensity line broadening and the hole depth at various hole burning frequencies has to be studied further for these materials in order to address the recording rate and storage capacity.

3.4 Ion Implanted Diamonds. Our project is mostly focused on optical characterization of some ion implanted natural diamonds as actual materials. These systems are outstanding materials due to their extreme hardness, have high frequency phonon spectra and dip electron traps. Therefore, they are good potential materials for high temperature, and non-volatile optical storage. We continued photoluminescence study of natural diamonds containing Xe impurity centers with zero phonon line at 813.7 nm (1.523 eV). Photoluminescence measurements have been performed at temperatures 1.3 - 300 K. Samples were annealed gradually (Dr. A.M. Zaitsev) at temperatures between 300 C and 1400 C with increment of 100 C. Subsequent

photoluminescence measurements were performed after each annealing cycle to investigate process of activation of Xe centers. No luminescence was observed at temperatures less than 800 C. As the annealing temperatures was increasing from 800 to 1400 C, the luminescence at 813.7 nm gradually amplified in all four samples. The most significant growth (about 25 times) was observed for sample with the list Xe ion implantation dose. This behavior may be explained by significance of nonradiative photoluminescence quenching in the most heavily implanted, and therefore, the most damaged samples. Father thermal annealing at 1500 C will be performed and photoluminescence and hole burning will be studied. Width of the zero-phonon line at 1.4 K was determined to be of 10 cm^{-1} . A weak phonon band was observed in the wavelength region 815 - 840 nm. This material is potentially interesting for high temperature optical storage and its investigation will continue.

Publications and presentations:

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